Electronic Supplementary Information (ESI) for

Efficient Two-terminal Artificial Synapse Based on a Network of Functionalized Conducting Polymer Nanowires

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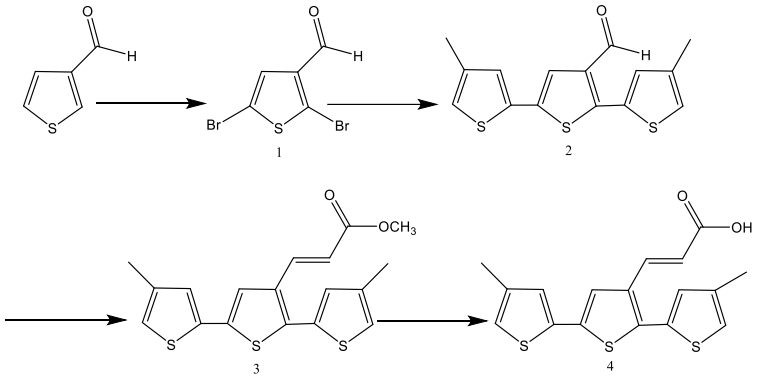
Synthesis



2,5-Dibromo-3-formylthiophene (1)

Thiophene-3-carboxaldehyde (2.61 g, 22.8 mmol) was mixed with 48% aqueous hydrobromic acid (6.8 mL), and ether (6 mL), then cooled at 0 °C. A mixture of bromine (7.36 g, 46.0 mmol) and 48% aqueous hydrobromic acid (6.8 mL) was added dropwise under vigorous stir. The reaction mixture was then heated at 50 °C and reacted for 4 h. After reaction, the mixture was diluted with water (100 mL) and extracted with ether (3×50 mL). The organic layers were combined, washed with 10% sodium thiosulfate solution (2×15 mL) and water (30 mL), and dried (Na_2SO4). The solvent was removed under reduced pressure to give dark crude product. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 5:1). (4.32 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) 9.80 (s, 1H, CHO), 7.34 (s, 1H).

4,4''-dimethyl-[2,2':5',2''-terthiophene]-3'-carbaldehyde (2).

2,5-dibromo-3-formylthiophene (1) (2.43 g, 9.0 mmol) and tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] (0.70 g, 0.6 mmol) was dissolved in 80 mL of 1,2-dimethoxyethane. 4-Methylthiophene-2-boronic acid (2.84 g, 20 mmol) and a solution of 1 M Na_2CO_3 (60 mL) were added. The reaction mixture was refluxed for 5 h. Then another portion of

4-methylthiophene-2-boronic acid (0.56 g, 4 mmol) was added and the reaction mixture was refluxed for overnight. The reaction mixture was concentrated under vacuum and 80 mL of dichloromethane was added. The organic residue was washed with water (2×25 mL), then dried (Na_2SO_4). Removing the solvent under vacuum gives the crude product. The crude product was dissolved in CH_2Cl_2/ hexane (1:1) and passed through a pad of silica to remove baseline material and the palladium catalyst. Further purification was carried out by column chromatography (hexane/ethyl acetate = 7:1), to give the compound (2) as a bright yellow solid (1.92 g, 70 %): ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) 10.08 (s, 1H, CHO), 7.51 (s, 1H, H 4'), 7.11 (s, 1H, H 3), 7.07 (s, 1H, H 3''), 7.02 (s, 1H, H 5), 6.86 (s, 1H, H 5''); 2.32 (s, -C<u>H</u>$_3$), 2.26 (s, -C<u>H</u>$_3$). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm) 185.20, 138.64, 137.41, 131.32, 127.08, 124.10, 121.95, 121.05, 15.64.

3-(4',4'''-dimethyl-[2',2'':5'',2'''-terthiophene]-3''-yl) acrylic acid methyl ester (3)

(Triphenylphosphoranylidene) methyl acetate (3.41 g, 10 mmol, 1.5 equiv) was added to the solution of (2) (2.1 g, 7.0 mmol) in anhydrous THF (250 mL). The reaction mixture was stirred at 50 ºC for 6 h and concentrated in vacuo to give a bright yellow solid, which upon purification by column chromatography on silica gel (hexane/ethyl acetate = 6:1) gave the product (3) (2.02 g, 80%)**.** ^{1}H NMR ($CDCl_3$, δ/ppm), 7.92 (d, 1H, C<u>H</u>=CHCOOCH$_3$), 7.28 (s, 1H, H 4''), 7.01 (s, 1H, H 3'), 6.99 (s, 1H, H 3'''), 6.95 (s, 1H, H 5'), 6.85(s, 1H, H 5'''), 6.35 (dd, 1H, CH=C<u>H</u>COOCH$_3$); 3.80 (s, -OC<u>H</u>$_3$), 2.31 (s, -C<u>H</u>$_3$), 2.27 (s, -C<u>H</u>$_3$); ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm) 167.64, 162.33, 138.78, 138.64, 137.51, 137.05, 136.79, 135.81, 133.41, 130.06, 126.75, 122.89, 121.67, 120.60, 118.70, 51.67, 15.72, 15.68.

3-(4',4'''-dimethyl-[2',2'':5'',2'''-terthiophene]-3''-yl) acrylic acid (MTAA) (4)

The compound (3) (1.04 g, 3 mmol) was dissolved in 30 mL of 1:1 (v:v) mixture of MeOH and 2 M aqueous NaOH and refluxed for 5 h. The reaction mixture was cooled to room temperature and methanol was removed in vacuum. The aqueous solution was acidified with 5 mol / L HCl to pH 3 and the precipitate was collected and dried in vacuum oven to give *(4)* as yellow powder. (0.83 g, 80%).; ^{1}H NMR (DMSO-d_6, δ/ppm), 7.76 (s, 1H, H 4'') 7.73 (d, 1H, C<u>H</u>=CHCOOH), 7.35 (s, 1H, H 3'), 7.24 (s, 1H, H 3'''), 7.16 (s, 1H, H 5'), 7.12 (s, 1H, H 5'''), 6.58 (dd, 1H, CH=C<u>H</u>COOCH$_3$); 2.26 (s, -C<u>H$_3$</u>), 2.22 (s, -C<u>H$_3$</u>); ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm) 167.66, 161.76, 138.46, 138.28, 135.86, 135.16, 134.73, 133.40, 132.53, 130.11, 127.08, 123.74, 122.61, 121.48, 120.97,15.24.

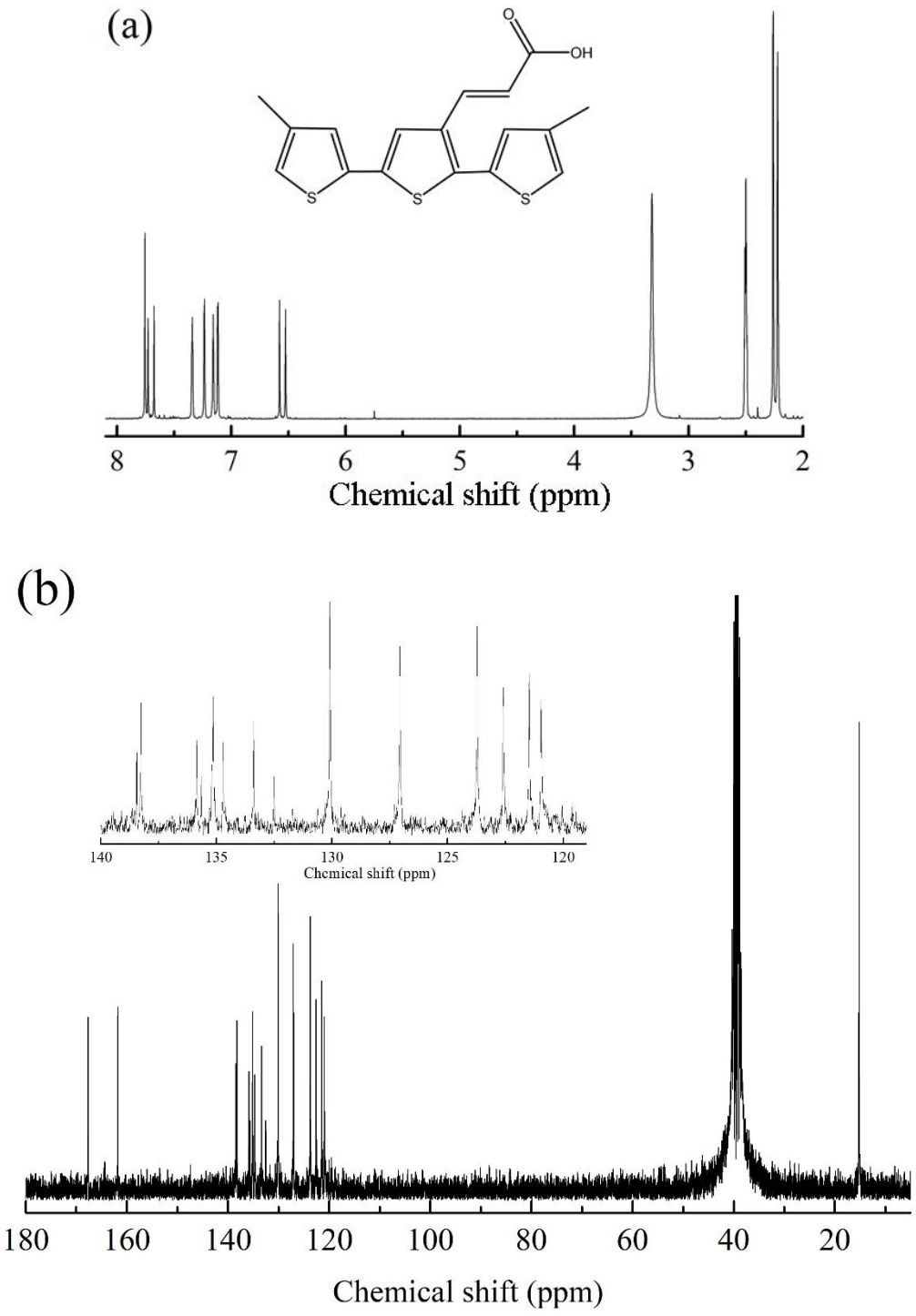


Fig. S1 ^{1}H and ^{13}C NMR spectra of MTAA.

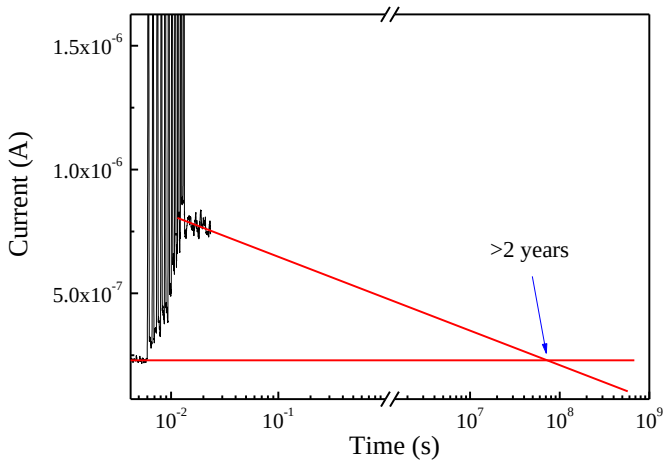


Fig. S2 Retention behaviors of the conductance state triggered by 10 electrical pulses.

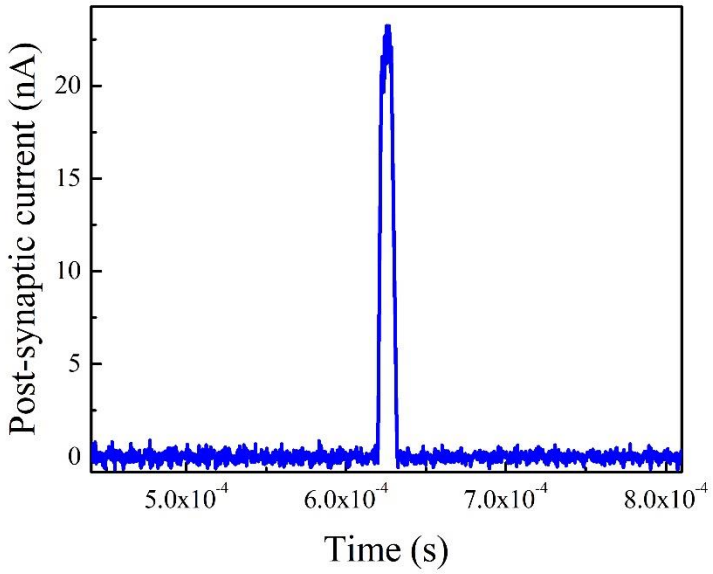


Fig. S3 EPSC triggered by an applied voltage pulse of 0.03 V with width of 10 μs.